#### EMISSIONI GASSOSE DIFFUSE IN AREE VULCANICHE. ASPETTI GEOCHIMICI, STRUTTURALI E MODELLI FISICI DEL PROCESSO. SVILUPPO DI TECNICHE DI MONITORAGGIO

#### Scientific Coordinator Giovanni Chiodini INGV- Osservatorio Vesuviano

## ACTIVITY REPORT -2nd YEAR

#### PROJECT PARTICIPANTS

RU#	AFFILIATION	RESPONSIBLE
1	INGV-sezione Osservatorio Vesuviano Na	Giovanni Chiodini
2	INGV-Roma1	Fedora Quattrocchi
3	Lab. Ing. Nucleare Montecuccolino Bologna	Domiziano Mostacci
4	Dip. CFTA Università.Palermo	Francesco Parello
5	I.G.G.I. CNR Pisa	Roberto Cioni
6	Dip. Sc Terra, Geol-Amb., Univ. Bologna	Todini Ezio (Micol Todesco)

#### GENERAL OBJECTIVES

The general objective of the project is: the development of a methodology for the monitoring of the diffuse degassing areas (DDS)

For the attainment of this objective, the project was originally divided in the following expected results for each project year (Tab 1):

Tab 1) Expected results for each project year (the achieved results are in bold black).

YEAR	EXPECTED RESULTS
	Thematic maps of the DDS at Solfatara, Mofete, Mt.Vesuvio, and Ischia (RU1; RU2,
Ι	RU4, RU5).
	Definition of appropriate geostatistical methodology (RU1, RU5).
	Set up of a method for the measurement of thermal energy released from hot grounds
	(RU1)).
	Analytical data of ${}^{14}$ C in the rings of a tree of Solfatara (RU3).
	Volcanological evolution of Solfatara (RU1).
	Physical modeling for the study of DDS's (RU1, RU6).
	Thematic maps of the DDS at Vulcano and Lipari (RU1; RU2, RU4, RU5)
II	Analytical data of ${}^{14}$ C and first consideration on the CO <sub>2</sub> degassing at the Solfatara in the last 20-30 years (RU3).
	Physical modeling for the study of DDS's, with special attention to the Solfatara (RU6,
	RU1).
	Thematic maps of the DDS at Pantelleria, Etna, and Nisyros (RU1; RU2, RU4, RU5).
III	Analytical data of ${}^{14}$ C and first consideration on the CO <sub>2</sub> degassing at the Solfatara in the last 20-30 years (RU3).
	Physical modeling for the study of DDS's, with special attention to Vulcano (RU6, RU1).

The expected results can be divided in the following tasks:

- (a) Task #1: thematic maps of DDS (diffuse degassing structures) of volcanic areas (CO<sub>2</sub> flux map, structural maps, <sup>13</sup>C data of soil gases, seismic studies of DDS, ecc)
- (b) Task #2: definition of appropriate geostatistical methodologies
- (c) Task #3: Set up of a method for the direct measurement of thermal energy released from hot grounds
- (d) Task #4: Physical modelling of the DDS (method) and specifically of Solfatara and Vulcano DDS
- (e) Task #5: <sup>14</sup>C measurements

## TASK # 1- Thematic maps of DDS

- RU PARTICIPANTS : RU1, RU2 and RU4
- 2nd YEAR OBJECTIVES

Thematic maps of Vulcano and Lipari

- 2nd YEAR RESULTS
  - **Methodology:** The main method applied to map the DDS is the accumulation chamber method for soil  $CO_2$  flux measurements. During 2002 an accumulation chamber method for the measurement of soil  $CH_4$  flux has been published. The so called 'Eddy correlation' method for the measurements of soil  $CO_2$  fluxes from large area has been experimented at Solfatara and the results have been published.
  - Data acquisition: According to the project Vulcano and Lipari were investigated during 2002. At Vulcano the campaigns regarded La Fossa crater (54 soil CO<sub>2</sub> flux and temperature gradient measurements) and the 'Porto di Levante' thermal area (203 soil CO<sub>2</sub> flux and temperature gradient measurements). At Lipari were selected two areas with macroscopic signs of degassing: 'Cava di Caolino' (141 soil CO<sub>2</sub> flux and temperature measurements) and 'La Fossa del Faurdo' (411 soil CO<sub>2</sub> flux and temperature measurements) areas. In addition continued the study of Solfatara where RU2 (in collaboration with RU1) performed a specific hydro-geochemical campaign while RU4 continued the study of the <sup>13</sup>C isotopic composition of soil CO<sub>2</sub>.
  - **Processing and interpretation:** the results of the 1<sup>st</sup> year campaigns and, partially, of the  $2^{nd}$  year campaigns have been processed with sequential Gaussian simulation algorithms (sGs method, see task# 2, RU1 report and ANNEX 1). Many of the maps elaborated are presented in ANNEX 1. The <sup>13</sup>C isotopic composition of soil CO<sub>2</sub> has been utilised to characterise the origin of CO<sub>2</sub> in the Solfatara area, to estimate the contributions from various sources (volcanic, organic, atmospheric, etc.), to recognise zones affected by diffusive flux (where carbon isotopic fractionation occurs) from zones affected by viscous flux.
  - **Other:** in addition to the original program, specific seismic and geo-electric investigations have been done in the areas of Solfatara and of Nisyros. Furthermore a new accumulation chamber for measurements of soil H<sub>2</sub>S fluxes has been set up and is under experimentation at Solfatara (RU1).

percentage of achievement on 20.12.02.	80%
percentage of achievement foreseen at the end of the project on 31.12.03	100%

## TASK # 2- Definition of appropriate geo-statistical methodology

• RU PARTICIPANTS : RU1 and RU5

## • 2nd YEAR OBJECTIVES

Set up of an appropriate geo-statistical method for the elaboration of the soil  $CO_2$  flux values. The aims are the mapping of DDS, the computation of total gas output, the estimation of the uncertainty and the definition of a suitable sampling density.

- 2nd YEAR RESULTS
  - **Methodology:** Two different approach have been used by RU1 and RU5. The two methods are detailed described in the RU1 and in RU5 reports (and in RU1-ANNEX1)
  - **Data acquisition:** different data sets have been used to test the methods.
  - **Processing and interpretation:** RU1 applied the geostatistical approach to data from volcanoes (RU1 report, ANNEX1), RU5 applied the method to data from landfill. The method and the results have been presented in international congress and elaborated for publications.
  - Other: RU1 worked on the statistical elaboration of data from automatic station FLXOV1 sited at Solfatara. The statistical analyses was aimed to separate the part of the signal linked to variations in the endogenous source of the CO2 flux, from the part controlled by environmental (soil and atmosphere parameters) changes. The results have been submitted for publication in EPSL.

percentage of achievement on 20.12.02.	80%
percentage of achievement foreseen at the end of the project on 31.12.03	100%

# <u>TASK #</u> 3- Set up of a method for the direct measurement of thermal energy released from hot grounds

- RU PARTICIPANTS : RU1
- 2nd YEAR OBJECTIVES

Set up of an appropriate method for the direct measurement of thermal energy released from hot grounds.

- 2nd YEAR RESULTS
  - **Methodology**: Two methods are under investigation: the first method consists on the using of a specific commercial sensor for soil heat flux measurement (LASTEM sensor method); a second approach consists in the systematic measurement of the thermal gradients of the DDS's soils. Finally during 2002 IR high resolution images have been tested as an other approach for the visualisation of the thermal anomalies associated with DDS.
  - Data acquisition: After the first year of field campaigns and laboratory tests, on January 2002 started a long period test of the 'LASTEM sensor method'. The sensor has been installed in the automatic CO2 flux station sited at Solfatara (FLXOV1). Since that period the sensor give a signal every two hours together with the thermal gradient recorded by three PT100 sensors installed at different depths in the soil. Infra-red images of DDS have been taken at Solfatara, Vesuvio, Vulcano and Nisyros (see ANNEX2)
  - **Processing and interpretation:** The data, together with CO2 fluxes and chemical compositions of the fumaroles, are under elaboration.

percentage of achievement on 20.12.02.	80%
percentage of achievement foreseen at the end of the project on 31.12.03	100%

**TASK # 4:** Physical modelling of the Diffuse Degassing Structures

• RU PARTICIPANTS : RU6 and RU1

#### 2nd YEAR OBJECTIVES

Aim of the Task #4 is the application of a physical model to the study of diffuse degassing. In particular, the second year was aimed at a comparison between available data and modelling result, with a special focus on the hydrothermal system of La Solfatara.

#### 2nd YEAR RESULTS

- Methodology: Numerical simulations were performed to study the role of deep fluid mixture injected at the base of a shallow hydrothermal system (i.e. the Solfatara hydrothermal system). All the simulations performed this year were performed with the TOUGH2 geothermal simulator with an equation of state (EOS) accounting for the contemporaneous presence of water and carbon dioxide. The model describes the coupled transport of heat and of a multi-phase fluid mixture, accounting for phase changes and latent and sensible heat effects.
- Data acquisition: All the simulations were performed according to a conceptual model that was developed on the basis of the available knowledge on the hydrothermal system of La Solfatara. Most of the necessary data derived from geothermal drilling and from the preexisting geochemical model and were acquired through a bibliographic research. Important constraints for our model derived from the more recent measurement campaigns, aimed at the evaluation of diffuse degassing from La Solfatara crater. These data were used to define the order of magnitude of deep inflow and to constrain the energy budget associated with diffuse degassing.
- Processing and interpretation: After appropriate tuning of the conceptual model, performed simulations could successfully reproduce some of the main features of the hydrothermal system at La Solfatara. These include: the observed degassing rate and energy release associated with diffuse degassing, the development of a shallow single phase region, whose existence and conditions match the predictions of the geochemical model, developed on the basis of independent data. These conditions were achieved by simulating a prolonged injection of a hot mixture of water and carbon dioxide at the base of a shallow hydrothermal system. These conditions were then applied as initial conditions to simulate chemical variations recorded during the most recent bradyseismic crises. Volcanic unrest was simulated imposing a higher fluid injection rate and a higher CO<sub>2</sub> content in the injected mixture. Appropriate choice of the periods of increased injection rate allowed us to match the observed compositional variations for the discharged fluids. A research article on these results has been recently submitted for publication (RU1 and RU5 ANNEX 2).
- Other: During this year, a new fruitful collaboration started with the Earth Science Division at the Lawrence Berkeley National Laboratory (California). This allowed us to extend the study to include the relations between hydrothermal fluid circulation and ground deformation. This aspect was not included in the original project, but the relevance of this topic to the study of a bradyseismic area, such as Phlegrean Fields, provided a strong motivation to modify previous planning.

percentage of achievement on 20.12.02. percentage of achievement foreseen at the end of the project on 31.12.03 100%

70%

## TASK # 5- C-14 measurements

• RU PARTICIPANTS : RU6

#### • 2nd YEAR OBJECTIVES

Investigate C-14 content abnormalities in trees exposed to massive release of fossil (hydrothermal) CO<sub>2</sub> in Solfatara area

#### • 2nd YEAR RESULTS

- **Methodology**: : extract cellulose from tree ring samples of years of interest and make into graphite. Measurement on AMS (on University of Arizona C14-dedicated mass spectrometer).
- **Data acquisition**: A pine tree was selected during the first year. The rings from years 1981, 82, 83, 84, 85 and 86 where treated.
- Processing and interpretation: waiting for results from AMS, measurements in progress.

percentage of achievement on 20.12.02.	25%
percentage of achievement foreseen at the end of the project on 31.12.03	100%(?)

#### • RESEARCH PRODUCTS OF THE PROJECT

- $n^{\circ}$  of articles published on international journals: 6 + (4 submitted)
- n° of articles published on national journals, proceedings, technical reports: 2
- invited papers and talks: 4
- Presentation at international meetings: 17
- Presentation at national meetings:5
- Data base: DDS data base (in progress)
- Computation codes:
- Other: Atlas of DDS (thematic maps, in progress)

PUBLICATIONS LIST (inclusive of papers in prints and accepted)

- Cardellini C., Chiodini G., Frondini F., Granieri D., Lewicki J. and Peruzzi.L. (2002) Accumulation chamber measurements of methane fluxes from natural environments and landfills. Applied geochemestry, 18, 45-54
- Chiodini G., Brombach T., Caliro S., Cardellini C., Marini L., Dietrich W. (2002) Geochemical evidences of an ongoing volcanic unrest at Nisyros Island (Greece) Geophys. Res. Letter , 29, 16.
- Todesco M., Neri A., Esposti Ongaro T., Papale P., Macedonio G., Santacroce R. e Longo A., (2002) Pyroclastic flow hazard at Vesuvius from numerical modelling. I. Large scale dynamics. Bull. Volcanol., 64, 155-177.
- Esposti Ongaro T., Neri A., Todesco M., Macedonio G., (2002) Pyroclastic flow hazard at Vesuvius from numerical modelling. II. Analysis of local flow variables. Bull. Volcanol., 64, 178-191.
- Todesco M., Chiodini G. e Macedonio G. (submitted) Monitoring and modeling hydrothermal fluid emission at La Solfatara (Phlegrean Fields, Italy). J. Volcanol. Geotherm. Res. (\*)
- Werner C., Chiodini G, Voigt D., Caliro S., Avino R., Russo M., Wyngaard J., Brantley S, (2002) Monitoring Volcanic Hazard Using Eddy Covariance at Solfatara Crater, Naples, Italy. EPSL (accepted).

Submitted paper

- Cardellini C, Chiodini G., and Frondini F (2002) Application of Stochastic Simulation to CO2 Flux from soil: Mapping and Quantification of Gas Release. Submitted at JGR
- G.Chiodini, R.Avino, T. Brombach, S. Caliro, C. Cardellini, S. De Vita, F. Frondini, M. Enrica, G. Ventura. (2002) Fumarolic degassing west of M.Epomeo, Ischia (Italy) Submitted at JVGR
- Chiodini, Todesco, Caliro, Del Gaudio, Macedonio, Russo (2002) Magma degassing as a trigger of bradyseismic events: the case of Phlegrean Fields (Italy). Submitted to GRL
- D. Granieri, G. Chiodini, W. Marzocchi, R. Avino (2002) Continuous monitoring of CO2 soil diffuse degassing at Phlegraean Fields (Italy): influence of environmental and volcanic parameters. Submitted at EPSL

#### Notes of the coordinator

#### **Positive highlights**

I am very happy of the results obtained by each task with the only exception of task 5. In particular the work done jointly by RU1 and RU6 in the frame of the task 4 gave very positive results, opening a new field of investigation, i.e. physical modelling of the Diffuse Degassing Structures, which in my opinion can lead to important results in the study of the pre-eruptive conditions of volcanic systems.

#### Negative points.

The task 5 is significantly delayed with respect to the original program. Even if a method for the preparation of the wood samples of trees has been set up, however we are still waiting the first analytical results. The RU3 responsible ensured me that the first results will be available in January. I ask the commission to wait until the end of January before deciding the 3<sup>rd</sup> year cost of RU3.

## EMISSIONI GASSOSE DIFFUSE IN AREE VULCANICHE. ASPETTI GEOCHIMICI, STRUTTURALI E MODELLI FISICI DEL PROCESSO. SVILUPPO DI TECNICHE DI MONITORAGGIO

#### RU #1 Responsible Giovanni Chiodini

INGV- Osservatorio Vesuviano

# ACTIVITY REPORT-2nd YEAR

#### RU PARTICIPANTS

Name-Position	Affiliation	man/month
Giovanni Chiodini researcher	OV-INGV	5
Rosario Avino technician	OV-INGV	4
Pier Paolo Bruno researcher	OV-INGV	1.0
Stefano Caliro researcher	OV-INGV	4
Carlo Cardellini phD-student	Università Perugia	6
Francesco Frondini reseracher	Università Perugia	2
Danilo Galluzzo researcher	OV-INGV	1.5
Domenico Granieri researcher	OV-INGV	4
Mario La Rocca researcher	OV-INGV	1.5
Warner Marzocchi	OV-INGV	1
Lavinia Perrotta borsista	OV-INGV	8
Massimo Russo technician	OV-INGV	4
Gilberto Saccorotti researcher	OV-INGV	0.5
Guido Ventura researcher	OV-INGV	3

## **1. 2nd YEAR OBJECTIVES**

The general objective of the project is the development of a methodology for the monitoring of the diffuse degassing areas (DDS). For the achievement of this main objective, the contribution of the OV-INGV RU during the 2nd year regarded the following different aspects: 1) development of an appropriate geo-statistical tool for the analyses of the soil  $CO_2$  flux data; 2) development of a method for the measurement of the heat flux associated with soil diffuse degassing of hydrothermal fluids; 3) acquisition of the campaign data for Vulcano and Lipari areas and elaboration and interpretation of the data acquired during the 1st year project (Solfatra, Vesuvio and Ischia); 4) structural and seismological features of DDS; 5) Physical numerical modelling of Solfatra DDS (in collaboration with the RU UniBo, Todesco)

#### 2. 2nd YEAR RESULTS

#### 2.1 methodologies

#### 2.1 Geo-statistical tool for the elaboration of soil CO<sub>2</sub> flux data (sGs approach)

Conditional sequential Gaussian simulations (sGs) have been applied for the first time to the study of soil diffuse degassing. The application regards many data set of soil CO2 fluxes measured with the accumulation chamber methodology at volcanic areas. The sGs algorithm was used to generate 100 simulations of CO2 flux for each area. Probabilistic summaries of these simulations, together with the information given by the probability plots, were used (i) to draw maps of the probability that CO2 fluxes exceed thresholds specific for a background flux, i.e., to define the probable extension of the degassing structures, (ii) to calculate the total CO2 output, and (iii) to quantify of

the uncertainty of the estimation. The results show that the sGs is a suitable tool to study soil diffuse degassing, producing realistic images of the distribution of the CO2 fluxes that honor the statistics of the original data. Moreover the relation between the sample design and the uncertainty of estimation was investigated founding an empirical relation between uncertainty and the sampling density, that can usefully used for the planning of future CO2 flux surveys.('Cardellini, Chiodini and Frondini Application of Stochastic Simulation to CO2 Flux from soil: Mapping and Quantification of Gas Release, submitted to JGR, in revision, ANNEX 1, Part I).

# 2.1.2 Method for the measurement and for the monitoring of the heat flux associated with soil diffuse degassing

Different methods are under investigation. A first method consists on the using of a specific commercial sensor for soil heat flux measurement (LASTEM sensor). After the first year of experiments (field campaigns and laboratory tests), a long period test started on January 2002 when the sensor has been installed in the automatic  $CO_2$  flux station sited at Solfatara. Since that period the sensor give a signal every two hours together with the thermal gradient recorded by three PT100 sensors installed at different depths in the soil. A second approach consisted in the systematic measurement of the thermal gradients of the DDS's soils (Solfatara, Nisyros, Ischia and Vulcano). The data, together with  $CO_2$  fluxes and chemical compositions of the fumaroles, are under elaboration. Finally during 2002 IR high resolution images have been tested as an other approach to the visualisation of the thermal anomalies associated with DDS of Solfatara, Vesuvio, Vulcano and Nisyros (see ANNEX2).

#### 2.2 Data acquisition

During 2002 continued the acquisition of new data (soil  $CO_2$  flux, soil temperatures, thermal gradients and structural data) from the active volcanoes of Italy and from the Nisyros volcano. According to the original project Vulcano and Lipari have been investigated. A synthesis of the data acquired in the framework of the GNV project or available for the project is described in Table 1. In the case of Solfatara and Ischia the data have been jet published, or submitted for publication. The other set of data are under elaboration.

Volcano	area	n. of $CO_2$ flux (and soil	n. of thermal	structural	Year
		temp.)	gradients	study	
Campi Flegrei	Solfatara (*)	406	-	-	1998
Campi Flegrei	Solfatara (*)	430	100	YES	2000
Campi Flegrei	Mofete	178	-	-	2000
Vesuvio	Cone	865	-	YES	2000 - 2001
Ischia	Donna Rachele	336	30	YES	2001
Lipari	Valle del	411	-	YES	2002
	Fuardo				
Lipari	Cava Caolino	141	-	YES	2002
Vulcano	Fossa Grande	600	54	YES	1998-2002
Vulcano	spiaggia	203	203	-	2002
Nisyros	Lakki plain (*)	2883	100	YES	1999-2002

Table 1 Data acquired (or available) in the framework of GNV project

(\*) co-financed by UE project GEOWARN

#### 2.3 Data processing and interpretation

Soil  $CO_2$  flux, temperature and thermal gradient of the investigated DDS have been elaborated trough the sGs approach. The aim is the production of thematic maps of DDS and the computation of the total  $CO_2$  emission and of the associated thermal energy. The data of Solfatara have been jet published, the data of Ischia have been submitted for publication in JVGR while the data of the other areas are under processing. Preliminary elaboration for each investigated area are reported in ANNEX 1 Part II, together with structural maps (Ischia and Solfatara) and IR images of degassing structures (Solfatara, Vesuvio and Vulcano).

#### 2.4 Others

Specific seismological investigations have been carried out at Solfatara and at Nisyros. In the case of Nisyros a paper comprehensive of structural, seismological and geochemical data is in elaboration.

The soil CO<sub>2</sub> flux and the thermal energy output from Solfatara DDS (diffuse degassing structure) have been used to constrain the physical-numerical model of the hydrothermal system which feed the Solfatara manifestation (Todesco et al., 2002). This work has been done in strict collaboration with Micol Todesco (RU UniBO). Numerical simulations, carried out using TOUGH2 code, describe the ascent and evolution of a hot multi-phase and multi-component fluid, made out of water and carbon dioxide, through a homogeneous porous medium. Selected system properties and conditions allowed the reproduction of some of the main features characterizing the natural system, including the energy budget associated with the ascent and condensation of hot fluids, and the development of a single-phase gas region, whose existence was inferred based on independent chemical data. Subsequently the model has been used to simulate the chemical variations of the fumarolic fluids during the bradyseismic crisis of Campi Flegrei. The results suggest a primary role of magma degassing in driving unrest episodes of the volcanic system (ANNEX 2, draft of :Chiodini, Todesco, Caliro, Del Gaudio, Macedonio, Russo (2002) Magma degassing as a trigger of bradyseismic events: the case of Phlegrean Fields (Italy). Submitted to GRL)

#### **3. RESEARCH PRODUCTS**

- articles published on international journals n. 4 (+ 4 submitted, see below)
- $\cdot$  n° of articles published on national journals, proceedings, technical reports n. **1**

Chiodini G. - The Hydrothermal Systems of Vesuvio and Campi Flegrei. Proceedings of Workshop-Short Course on Volcanic Systems Geochemical and Geophysical Monitoring. Melt inclusions: methods, applications and problems. September 26-30th, 2002 Seiano di Vico Equense – Napoli, Italy

- invited papers and talks n. 2

Chiodini G. - Geochemical surveillance at Phlegrean Fields and Mt Vesuvius. Scuola di Geochimica, Monitoraggio dell'attività Vulcanica e Sismica. Palermo 14-18 Ottobre 2002
Chiodini G. - "Natural CO<sub>2</sub> emission in Italy" held at the LBNL on July 26, 2002.

- Bruno, P.P.; Godio, A.; Bais, G.; Chiodini, G.; Di Fiore, V.;Strobbia, C. (2002) Shallow structure of the Solfatara volcano by multisource geophysical data. EGS XXVI General Assembly, 2002 Nice (France)
- Cardellini C., T. Brombach, S. Caliro, G. Chiodini, F. Frondini, S. Giaquinto, F. Parello (2002) Input of deeply derived carbon dioxide in southern Apennine regional aquifers (Italy) EGS XXVI General Assembly, 2002 Nice (France), EGS02- A 05731
- Chiodini G., R. Avino, T. Brombach, S. Caliro, C. Cardellini, Frondini (2002) New data on the fumarolic emission at Ischia (Italy) EGS XXVI General Assembly, 2002 Nice (France), EGS02- A 06104

<sup>-</sup> presentations at international meetings n. 12

Avino R., Caliro S., Chiodini G., Del Gaudio C., Di Matteo V., Pece R., Russo M. (2002) Geochemical monitoring in Campi Flegrei from 1970 - 2000. - EGS XXVI General Assembly, 2002 Nice (France)

- Chiodini G., T. Brombach, S. Caliro, C.Cardellini, Luigi Marini, Volker Dietrich (2002) Geochemical variations indicating changing hydrothermal activity at Nisyros Island (Greece) EGS XXVI General Assembly, 2002 Nice (France), EGS02- A 06068
- Chiodini G., Saccorotti, Ventura (2002). Geochemical, sesimological and structural features of Diffuse Degassing Structures. M.te Pelee 1902-2002, IAVCEI Meeting, Martinica, Maggio 2002
- Galluzzo D., La Rocca M., Saccorotti G., Chiodini G. (2002) "A Seismic survey on Nisyros Island (Greece)" Primer Centenario del Observatorio de Cartuja - I.A.G. 8-11 October 2002,Poster Session, Parque de las Ciencias, Granada
- Granieri D., Chiodini G., Marzocchi W (2002). Continuous monitoring of CO2 soil diffuse degassing in volcanic sites:influence of environmental and volcanic parameters. The case of Solfatara and Vesuvius volcanoes (Naples, Italy) -EGS XXVI General Assembly, 2002 Nice (France)
- Saccorotti G., La Rocca M., Ponziani F., Galluzzo D., Chiodini G. (2002). The Seismic Signature of Degassing Structures: Two Examples from Solfatara and Nisyros Volcanoes -EGS XXVI General Assembly, 2002 Nice (France)
- Todesco M., Chiodini G., Macedonio G. (2001). Monitoring and modelling diffuse gas emission from volcanic areas. An interdishiplinary approach to improve our understanding of hydrothermal system evolution. AGU 2001 Fall Meeting, S. Francisco, 10-14 dicembre 2001.
- Werner C., Chiodini G, Voigt D., Caliro S., Avino R., Russo M., Wyngaard J., Brantley S, (2002) Monitoring volcanic fluxes using eddy covariance at Solfatara volcano, Naples, Italy Goldschmidt Conference Abstracts Volume, Davos, Switzerland, 18-23 August 2002.
- Werner C., Chiodini G, Brantley S, (2002) The use of Eddy Covariance in Monitoring Volatile and Heat Fluxes at Solfatara Volcano, Naples, Italy. Eos Trans. AGU, 83(47), Fall Meet. Suppl., Abstract : V22C-12, 2002

presentations at national meetings n. 1

Galluzzo D., La Rocca M., Saccorotti G., Chiodini G (2002)."Una campagna di acquisizione dati sismici a Nisyros (Grecia)" 21° Convegno Nazionale GNGTS, Roma 19-21 novembre 2002

#### PUBLICATIONS LIST (inclusive of papers in prints and accepted)

- Cardellini C., Chiodini G., Frondini F., Granieri D., Lewicki J. and Peruzzi.L. (2002) Accumulation chamber measurements of methane fluxes from natural environments and landfills. Applied geochemestry, 18, 45-54
- Chiodini G., Brombach T., Caliro S., Cardellini C., Marini L., Dietrich W. (2002) Geochemical evidences of an ongoing volcanic unrest at Nisyros Island (Greece) Geophys. Res. Letter, 29, 16.
- Werner C., Chiodini G, Voigt D., Caliro S., Avino R., Russo M., Wyngaard J., Brantley S, (2002) Monitoring Volcanic Hazard Using Eddy Covariance at Solfatara Crater, Naples, Italy. EPSL (accepted).
- Todesco M., Chiodini G. and Macedonio G. Monitoring and modelling hydrothermal fluid emission at La Solfatara (Phlegrean Fields, Italy). (2002) An interdisciplinary approach to the study of diffuse degassing. JVGR (accepted (\*)).

(\*) The paper was presented for a special issue of JVGR. It already went through the reviewing process and is accepted with minor revision, but the final decision of the editor on the entire special volume is still not official.

#### Submitted paper

- Cardellini C, Chiodini G., and Frondini F (2002) Application of Stochastic Simulation to CO2 Flux from soil: Mapping and Quantification of Gas Release. Submitted at JGR
- G.Chiodini, R.Avino, T. Brombach, S. Caliro, C. Cardellini, S. De Vita, F. Frondini, M. Enrica, G. Ventura. (2002) Fumarolic degassing west of M.Epomeo, Ischia (Italy) Submitted at JVGR
- Chiodini, Todesco, Caliro, Del Gaudio, Macedonio, Russo (2002) Magma degassing as a trigger of bradyseismic events: the case of Phlegrean Fields (Italy). Submitted to GRL
- D. Granieri, G. Chiodini, W. Marzocchi, R. Avino (2002) Continuous monitoring of CO2 soil diffuse degassing at Phlegraean Fields (Italy): influence of environmental and volcanic parameters. Submitted at EPSL

#### RU #2 Responsible Fedora Quattrocchi

INGV- Section Roma 1 – Laboratory of Fluid Geochemistry (INGV-LGFRM1)

# ACTIVITY REPORT-2nd YEAR

#### RU PARTICIPANTS

Name-Position	Affiliation	man/month
Fedora Quattrocchi, researcher	INGV-LGFRM1	2
Gianfranco Galli, researcher	INGV-LGFRM1	1
Luca Pizzino, researcher	INGV-LGFRM1	3
Nunzia Voltattorni, researcher	INGV-LGFRM1	3
Daniele Cinti, fellowship	INGV-LGFRM1	3
Luigino Piccolini, technician	INGV-LGFRM1	1

#### • 2nd YEAR OBJECTIVES

The main objectives as regards the groundwater study were i) to deepen the origin and evolution of the discharging fluids and ii) to quantify the various degree of the gas-steam-rock interaction and the geochemical processes accounting for their final chemical features.

The main objectives as regards the soil-gases study were i) to deepen the origin and evolution of the soil gas fluxes and concentrations of major and minor species ( $CO_2$ ,  $CH_4$ ,  $H_2S$ , Rn, He, etc...) and ii) to quantify the mass flux at surface, also the role of discontinuities and steam behavior as well as to compare the INGV-OV with the INGV-LGFRM1 methods on field (IR-spectrometry-short term measurements with portable gas-chromatography long term measurements, respectively), taking in consideration also minor gas species fluxes by the INGV-LGFRM1 methods.

#### • 2nd YEAR RESULTS

#### *Groundwater chemistry*

A total of 33 groundwater samples (springs, wells and gaseous wet pools) have been collected in the Solfatara volcano and surrounding areas (Pozzuoli, Cuma-Cigliano, Agnano, Bagnoli and Astroni) in order i) to deepen the origin and evolution of the discharging fluids, ii) to quantify the various degree of the gas-steam-rock interaction and the geochemical processes accounting for their final chemical features.

In the field, physico-chemical parameters (temperature, pH, Eh, electrical conductivity), bicarbonate content (by titration), H<sub>2</sub>S content (by colorimetric method) and dissolved radon (by  $\gamma$  spectrometry) have been measured. In laboratory, major elements (Ca, Mg, Na, etc, by liquid chromatography), minor and in trace elements (B, As, Sb, Hg, Li, SiO<sub>2</sub>, Br, Mn, Fe, etc., by ICP-Mass Plasma) have been analysed on all samples. Moreover, 15 samples have been collected for the analyses of <sup>87</sup>Sr/<sup>86</sup>Sr ratio and <sup>13</sup>\deltaC. Dissolved gas analyses have been performed on 25 water samples.

For a better interpretation of the obtained results and for emphasising eventual chemical anomalies

between them, samples have been grouped in 6 geographic families. The geochemical classification

of the sampled groundwater may be highlighted by the Ludwig-Langelier diagram (Fig. 1), as

follows:

• Na-Cl waters: in this group we find the samples Hotel Tennis, Tufano, Carannante and Capriccio (belonging to the Solfatara-Agnano family), Puteolane and Serapide (belonging to the Pozzuoli family), as well as some samples of the Agnano family (Agnano Sprudel and others). These waters are characterized by a very high electrical conductivity (up to 20 mS/cm) and high discharge temperatures (up to 85°C, as in the Hotel Tennis well). The only exception is represented by the Tufano well, being less mineralised (electrical conductivity equal to 3 mS/cm) and colder (temperature of 22.4°C) with respect to the above mentioned samples. The origin of these waters may be due to i) a huge mixing with seawater for the samples located along the Tyrrhenian coast (Tempio di Serapide and Terme Puteolane), ii) various degrees of mixing between cold shallow aquifers and hot deep brines (Agnano-Solfatara area); iii) mixing between deep brines and shallow steam-heated aquifers (Hotel Tennis), where is maximum the steam-input.

• Na-HCO<sub>3</sub> waters: in this group we find the bulk of the waters belonging to the Agnano family, samples located in the Cuma-Cigliano, Astroni and Bagnoli areas, and the Tortorelli well of the Pozzuoli family. All samples show relatively high saline contents (values of electrical conductivity ranging from 2 to 5 mS/cm) and temperatures spanning from18 to 57°C). The origin of these waters may be due to the interaction of CO<sub>2</sub>-rich fluids with the young vulcanites cropping out extensively in the area. In some cases (Tortorelli sample) the high temperature and the very peculiar chemical features (very low content of Ca and Mg, high bicarbonate and alkaline pH) are due to the interaction between gas, steam and shallow clayey strata, with both precipitation of carbonatic species at the permeability barriers and cationic exchange processes.

• Sulphate-acid waters: in this group we find samples of the Solfatara-Agnano area (Fangaia and Pisciarelli). These waters shows electrical conductivity values of 3-8 mS/cm and very high discharges temperatures (57-74°C). They are typical acid waters (pH = 2) whose origin is due to the dissolution of steam and reducing gases into shallow aquifers; the sulphate signature is due to the oxidation of the H<sub>2</sub>S.

• Ca-SO<sub>4</sub> waters: this chemistry is showed only by the Pozzo Solfatara sample, located inside the homonymous volcano. This water shows an electrical conductivity value of 3 mS/cm and a discharge temperature of 89°C, the hottest found in the area. Its chemistry may be due to the mixing between hot steam and reducing gases and Ca-SO<sub>4</sub> rich fluids.

## Fluxes and concentrations in soil gases

In the Solfatara volcano area 32 gas flux measurements were made by using the method of accumulation chamber (0.5 m x 0.5 m size). The analyses were performed directly in the field by using a portable gas cromatographer. The analysed gases are:  $CO_2$ ,  $H_2S$ , and  $CH_4$ . Radon determination was accomplished with a portable RAD 7 Durridge Radon Detector.

During the flux measurements, 32 soil-gas samples were collected using a 1 m stainless steel probe fitted with a brass valve. Some soil gas samples were collected and stored in metallic containers for laboratory analysis, for both a comparison with field measurements and He determination, not available in the field. Rn and Th measurements were made in a more extended area, all around the Solfatara volcano.

Some statistical parameters relative to the flux measurements are listed in table 1: it is interesting to note that the  $CO_2$  flux is meanly 1127.32 gr/m<sup>2</sup>\*d, although highest flux values were found in the "Fangaia" area and close to the so called "Bocca Grande". Radon flux distribution is very similar to the  $CO_2$  one: both gases have a dominant flux in a NE-SW direction and in minor part both in E-W and NW-SE directions.

|--|

			-		
Gas	Samples n°	Min value	Max value	Mean	Stand. Dev.
$CO_2 (gr/m^2*d)$	32	83.3	5287.20	1127.32	1394.99
$CH_4 (mgr/m^2*d)$	32	0	1524.96	361.49	481.30
$H_2S$ (gr/ m <sup>2</sup> *d)	32	0	390.24	28.34	89.84
$Rn (Bq/m^2*d)$	32	0	92763.87	18234.52	21372.40



Ludwig-Langelier diagram of the waters collected in the Campi Flegr

Fig. 1

The H<sub>2</sub>S flux measurements highlighted a NW-SE anomalous trend and a local spot with values > 100 gr/  $m^2_*d$ , in front of the "Stufe"area. CH<sub>4</sub> flux shows a trend quite different from the other gases: it is possible to distinguish NW-SE, N-S and E-W anomalous trends with local fluxes > 1000 gr/  $m^2_*d$ .

Results from soil gas samples analysed both in the field and in the laboratory for concentration measurements are in agreement with gas flux results (Fig. 2). Local trends are very similar, although soil-gas concentrations show a more diffusive distribution, as it was reasonable to suppose.



**Fig.2**: Comparison between  $CO_2$  flux and  $CO_2$  soil gas concentration. It is well evident that, in spite of a more diffusive distribution of soil gas concentration, principal trends of anomalous values are very similar.

#### • RESEARCH PRODUCTS

- $n^{\circ}$  of articles published on international journals = 0 (2 in preparation)
- $n^{\circ}$  of articles published on national journals, proceedings, technical reports = 1
- invited papers and talks= 0
- presentations at international meetings= 0
- presentations at national meetings = 2
- Data bases = YES
- Computation codes = NO
- Other = YES isoconcentration and isofluxes maps both for soil gas and groundwater

PUBLICATIONS LIST (inclusive of papers in prints and accepted)

 Quattrocchi F., Angelone M., Cinti D. Galli G., Pizzino L. (2001) Detailed study of Campi Flagrei circum-crateric aquifer: minor and trace elements. Atti Convegno Annuale GNV 2001, Roma 9-11- Ottobre, pg. 11-12.

#### RU#3 Responsible Domiziano Mostacci,

Associate Professor Università degli Studi di Bologna

# ACTIVITY REPORT-2nd YEAR

#### RU PARTICIPANTS

Name-Position	Affiliation	man/month
Domiziano Mostacci, Associate Professor	Università degli Studi di Bologna	5
Vincenzo Molinari, Full Professor	Università degli Studi di Bologna	1
Francesco Teodori, Research Fellow	Università degli Studi di Bologna	2
Roberto Giampieri, Research Specialist	ENEA	2

## • 2nd YEAR OBJECTIVES

investigate C-14 content abnormalities in trees exposed to massive release of fossil CO2. Measurements to be conducted on approx. 20 to 30 samples.

- 2nd YEAR RESULTS (max 1 page)
  - <u>Methodologies</u>: extract cellulose from tree ring samples of years of interest and make into graphite. Measurement on AMS (on University of Arizona C<sup>14</sup>-dedicated mass spectrometer)
  - Data acquisition: rings from years 1981, 82, 83, 84, 85 and 86 where treated.
  - Data processing and interpretation: waiting for results from AMS measurements in progress
  - Others: none
- RESEARCH PRODUCTS
  - n° of articles published on international journals: none
  - n° of articles published on national journals, proceedings, technical reports: none
  - invited papers and talks: none
  - presentations at international meetings: none
  - presentations at national meetings: none
  - Data bases : none
  - Computation codes : none
  - Other: none

#### **RU #4 Responsible Francesco Parello**

Position Prof.Associato Affiliation Dipartimento C.F.T.A. Università di Palermo

# ACTIVITY REPORT-2nd YEAR

#### RU PARTICIPANTS

		man/month
F. Parello Prof. Associato	Dipartimento C.F.T.A. Università di Palermo	4
A.Pisciotta - dottorando di ricerca	Dipartimento C.F.T.A. Università di Palermo	6
C. Federico-assegno di ricerca	INGV sez. Pa	3

#### • 2nd YEAR OBJECTIVES

• The carbon isotopic composition of CO2 is utilized in order to characterize the origin of CO2 and estimate the contributions from various sources (volcanic, organic, atmospheric, etc.) in the Solfatara area (Pozzuoli).

#### • 2nd YEAR RESULTS

On the base of a grid of more than one hundred points, we measured the temperature at 50 cm depth and the CO2 concentration. At the same time, the flux of CO2 was measured by the accumulation chamber method. Furthermore, at each site samples for chemical and isotopic analyses were also collected.

Moreover, in some selected sites we collected samples at different depths (25, 50, 75 and 100cm), to assess the natural processes taking place during the upraise of  $CO_2$  from the saturated layer (100% of  $CO_2$ ) to the atmospheric zone (100% of Air).

Data reveal the existence of a huge thermal anomaly inside the Solfatara area also characterised by high CO<sub>2</sub> flux. Moreover, in the main exhaling area, isotopic data ( $\delta^{13}C_{CO2}$ ) display values very similar to the signature of Bocca Grande fumarolic area. In the mean time isotopic fractionations are highlighted in the peripheral area, due to a large variety of natural processes taking place either at equilibrium or kinetically controlled.

Carbon dioxide concentrations and  $\delta^{13}C_{CO2}$  measured at different depth in the soils show a close relationship. due to a diffusive flux of CO<sub>2</sub> from the saturated layer (100% CO<sub>2</sub>) towards the atmosphere and to a complementary diffusion of air towards the CO<sub>2</sub> saturated layer. Heavy isotopes diffuse slower, leading to  $\delta^{13}C_{CO2}$  increase towards the surface proportionally to air dilution. The fractionation observed was almost 4.4 ‰, corresponding to the maximum theoretical values utilising the diffusion equation modified for isotope carbon species. The same process is also invoked for the oxygen isotope composition; in this case theoretical value, around 17‰, matches the observed trend.

#### • RESEARCH PRODUCTS

- presentations at national meetings; congress GNV 2001

#### **RU#5 Responsible Roberto Cioni**

Position: senior researcher

IGG-CNR, PI (Istituto di Geoscienze e Georisorse-CNR, Pisa)

# ACTIVITY REPORT-2<sup>nd</sup> YEAR

#### PARTICIPANTS TO THE RESEARCH UNIT

Name-Position	Affiliation	Man/month
Roberto Cioni – Senior Researcher	IGG-CNR,PI	3
Massimo Guidi – Researcher	IGG-CNR,PI	3
Raco Brunella – Researcher	IGG-CNR, PI	3
Lelli Matteo – contract	IGG-CNR, PI	2

#### • 2nd YEAR OBJECTIVES

Study of the effects of the sampling grid size on isoflux maps and on the flux value calculated over the entire area of the Solfatara. Set up of a methodology to evaluate the best strategy of sampling to obtain the best map and the minor error on the global flux estimation.

#### • 2nd YEAR RESULTS

The main purpose of the research is to set up a procedure suitable for a correct estimation of total soil gas flux diffused over a large area by means of punctual measurements or, more exactly, carried out over a support, which is small as compared to the entire area. As there have been problems in transferring funds from OV-NA to IGG-CNR we were forced to postpone the foreseen field work at Vulcano in January 2003. For this reason, in order to achieve the project objectives we performed a soil gas survey on a landfill located in the area of Pisa.

The utilized grids were a 10x10 m for a total of 608 samples and a 25cmx25cm grid over a sufficiently small area for a total of 900 samples. The gas flux has been determined by measuring the  $CO_2$  concentration versus time by means of an accumulation chamber method (Chiodini et al., 1998 and references therein).

Carbon dioxide fluxes have been mapped after data processing with ISATIS program, employing the kriging method (Clark, 1979 and references therein) to extrapolate values where the measures have not been taken. The extrapolation requires the construction of the ideal variogram from the experimental variogram, and the singling out of the best neighborhood to be considered for the interpolation process.

Moreover, the kriging method assures that the interpolated value is unbiased as compared to the mean value and the minimum variance (Wackernagel, 1995).

Nevertheless the global estimation of  $CO_2$  has not be done by utilizing the kriging technique. The global mean would in fact very rarely be kriged directly due to two main reasons (Journel and Huijbregts, 1978):

- 1. It is not usually possible to assume stationarity or a single drift of known form over the entire area, but only over limited neighborhoods (local quasi-stationarity).
- 2. Even if stationarity could be verified over the entire investigated area, there are usually too many data to construct a kriging matrix and then to solve the kriging system.

Moreover, the construction of such a kriging matrix would imply that the structural function, C (h) or  $\gamma$ (h), is known for distance h of the order of dimensions of the area and the limit of reliability of an experimental semi-variogram is a distance L/2, half of the field dimensions.

In order to estimate the total  $CO_2$  output from soil the method described by Chiodini et al. (1988) with the Sinclair (1974, 1991) procedure and the Sichel's t-estimator (Sichel, 1966, David, 1977) has been used. This methodology allows to calculate the mean flux and the confidence interval. Moreover the ratio between the samples belonging to the identified population and the total number of measurements provides also the portion of the surface that can be assigned to that population. It is therefore possible to determine the total flux and the variation interval with a 95% confidence.

Starting from the 10x10 m grid, four 20x20 m grids and nine 30x30 m grids have been constructed in order to have the maximum number of points for each grid. For each case the mean values and the confidence interval at 95% have been calculated with the previously mentioned procedure. The obtained results are shown in the attached table 1.

The same procedure has been utilised for the 25cmx25cm grid, 47 new grids with different number of sample (from 190 to 16) have been extracted but in this case also the "true" total flux value has been calculate. Data are reported in table 2.

These results clearly indicate the good agreement between the "true" value calculated by the integral and the values obtained by Sinclair procedure. This good agreement is respected if the number of sample is over 50, if the number of point is under this value we get too large error on the estimation. In others words the difference between the maximum and the minimum values increase noticeable (fig.1 and fig. 2) for that grid with number of samples less than 50.

The same results are more evident on the cartographic representation. It is important to underlying that, while for the global estimation we obtain satisfactory results also for grid with few samples, the same it is not true for the cartographic representation.

Conditional and not conditional simulations are under elaboration in order to verified how the distribution of fluxes, carried out by means of the kriging method, is representative and what is the variability of this phenomenon when we processing grids with a few number of samples. The conditional and not conditional simulation will be carried out by means of the highly specialised software ISATIS.

#### REFERENCES

Chiodini G., Cioni R., Guidi M., Marini L., Raco B. (1998). Soil CO2 flux measurements in volcanic and geothermal areas. Applied Geochemistry, 13, 543-552.

Clark I. (1979). Pratical Geostatistics. Department of Mineral Resources Engineering, Royal School of Mines, Imperial College of Science and Technology, London, 129p.

David M. (1977). Geostatistical ore reserve estimation. Elsevier Amsterdam.

Davis J. C. (1986). Statistics and Data Analysis in Geology. John Wiley & Sons, Inc. Second Edition, New York, 646p

Journel A.G., Huijbregts Ch. J., (1978) Mining geostatistics, Academic Press.

Sichel H.S., (1966). The estimation of means and associated confidence limits for small samples for lognormal population. Proc. 1966 Symp. South African Institute of Mining and Metallurgy.

Sinclair A.J., (1974). Selection of thresold values in geochimical data using probability graphs. Journal of Geochemical Explorat., 3, 129 – 149.

Sinclair A.J., (1991). A foundamental approach to thresold estimation in exploration geochemistry: probability plots revisited. Journal of Geochemical Explorat., 41, 1 – 22.

Wackernagel H., (1995). Multivariate geostatistics. Springer – Verlag, Berlin, 256p.

Sample	Total	Maximu	Minimu
#	flux	m	m
608	80029	87452	74342
151	82522	97512	72457
148	81701	89735	75989
156	81142	93942	73424
153	73317	83465	66480
68	86393	106188	73562
68	78887	93640	69614
67	72961	87640	64301
68	80439	101143	67506
69	87222	106534	76471
65	82603	100681	71435
67	82299	101763	71372
69	68983	81448	56328
67	59935	88932	52436

Table 1. Measured total, maximum and minimum fluxes for the considered Grid, starting from 10m x10 m.



Fig. 1. Number of samples vs total flux



Fig. 2. Number of samples vs difference between major and minor value for the total flux estimation

Table 2. Measured total, maximum and minimum fluxes for the considered Grid, starting from 25cm x25cm.

GRID	errore	Ftot	Мах	Min	number of
					samples
Integral	l value	74.	3		
total	14.	6 79.	0 84	.6 74.3	900
11	2 5.0	6 71.	4 81	.1 64.4	190
12	2 2.	5 65.	8 74	.3 60.3	190
33	2 11.	6 73.	3 80	.5 68.3	163
13	2 19.	2 70.	4 77	.2 65.6	180
21	2 1.	7 65.	6 72	.8 60.5	184
31	2 5.0	6 74.	2 84	.5 66.8	174
32	2 4.	1 76.	7 92	.8 65.6	174
11	3 2.3	3 63.	3 71	.0 52.9	87
12	3 2.3	3 78.	2 94	.2 68.8	86
13	3 0.0	6 70.	9 81	.2 64.5	78
21	3 1.	5 67.	6 83	.3 59.2	86
22	3 2.	1 63.	4 74	.9 55.5	86
23	3 2.8	8 77.	5 97	.2 65.0	78
31	3 1.9	9 63.	5 78	.8 53.6	82
32	3 2.3	3 81.	1 103.	.7 67.0	82
33	3 1.3	3 71.	2 88	.7 59.9	74
11	4 3.	1 76.	9 98	.7 60.0	46
12	4 0.	5 71.	4 88	.8 62.7	46
21	4 0.	5 56.	1 62	.5 42.5	46
22	4 1.2	2 /1.	2 94	.7 57.9	46
23	4 1.	b /1.	9 91	.6 60.1	46
31	4 2.2	2 66.	6 92.	.9 52.5	46
32	4 1.	5 60.	2 81	.4 48.5	46
33	4 2.7	1 73.	1 98	.4 59.0	46
11	5 0.3	3 57.	4 67	.7 48.0	33
12	5 0.0	o 52.	0 67	.5 43.8	33
21	5 0.0	60. 5 50.	1 90	.1 46.0	33
22	5 U.S	9 57.	0 81	.1 44.9	33
23	5 I./	2 49. C 57	0 69	.1 39.0	28
31	5 U.U	0 57. 4 50	Z 90. 4 71	.4 42.3	33
ు∠ ఎఎ	5 U.4	4 DZ. 1 54	4 / I.	.3 42.4	່ <u>ວວ</u>
33	5 I. 6 0.	1 54. 1 44	8 80. 2 50	.3 42.0	
11	0	1 44. 2 70	3 DU. 9 00	.1 34.0 5 56.2	
1Z 21	6 0.º	5 70. 1 55	0 99. 0 99.	.5 50.5	22
21	0 0. 6 0.	1 JJ. 8 40	Z 00. 7 64	.0 40.9	22
22	6 0.0	0 49. 1 51	7 04. 5 01	.0 41.0	18
20	6 0.4	+ 04. 7 70	ປີ ອີໄ 1 100	.i 39.0 1 /05	10
31	6 0.	1 10. 1 52	1 122. 1 QR	.i 49.0 7 /15	22
22	6 1.4	- 50. 2 61	1 11/	3 /51	· 22 22
11	σ 1. 7 Ω	ב ט <del>יו</del> . כ כפ	1 62	.5 <del>4</del> 5.1 6 29.4	<u> </u>
10	γ 0 7 Ο '	3 60. 3 62	1 00. <u>1</u> 22	.0 20.4 G /07	19 19
21	7 0.4	5 <u>59</u>	5 92	.2 45.2	18

227	1.2	55.9	91.0	41.2	18
237	0.6	57.3	88.0	43.7	18
327	0.7	60.3	93.1	46.0	16
337	1.0	62.8	84.9	51.7	16

#### PUBBLICATION

Cioni R., Guidi M., Raco B., Guercio M., Corsi R. (2002) CO2 flux from soil: a methodology to estimate the diffuse biogas. Proceedings of the 7<sup>th</sup> International Symposium on Environmental Issue and Waste Management in Energy and Mineral Production.

Cioni R., Guidi M., Raco B., Giamberini S., Daddi P. (2002). Measurement of biogas emissions from air soil interfacein the MSW landfill of Legoli (Pisa, Italy). Submitted to "Sardinia 2003" Ninth International Waste Management and Landfill Symposium, S. Margherita di Pula (Cagliari, Italy), 6-8 October 2003.

Cioni R., Guidi M., Lelli M., Raco B. (2001) Goestatistic techniques applied to the evaluation of flux errors: calculation of the total estimation variance of CO2 flux. Assemblea annuale del GNV (INGV), 9-10-11 ottobre 2001, Roma, Poster.

#### **RU#6 Responsible Prof. Ing. E. Todini**

Dip. Scienze della Terra e Geo-Ambientali Università di Bologna

## ACTIVITY REPORT-2nd YEAR

#### RU PARTICIPANTS

Micol Todesco,	Dip. Scienze della Terra e	12
Assegnista di Ricerca	Geo-Amb., Univ. Bologna	

#### • 2nd YEAR OBJECTIVES

Aim of the research unit is the application of a physical model to the study of diffuse degassing.

In particular, the second year was aimed at a comparison between available data and modelling result, with a special focus on the hydrothermal system of La Solfatara. Objectives for the second years also included the study of fractured system and a first approach to the inverse problem.

During this year, a new fruitful collaboration started with the Earth Science Division at the Lawrence Berkeley National Laboratory (California). This allowed us to extend the study to include the relations between hydrothermal fluid circulation and ground deformation. This aspect was not included in the original project, but the relevance of this topic to the study of a bradyseismic area, such as Phlegrean Fields, provided a strong motivation to modify previous planning.

#### • 2nd YEAR RESULTS

- **Methodologies**. Numerical simulations were performed to study the role of deep fluid mixture injected at the base of a shallow hydrothermal system. All the simulations performed this year were performed with the TOUGH2 geothermal simulator with an equation of state (EOS) accounting for the contemporaneous presence of water and carbon dioxide. The model describes the coupled transport of heat and of a multi-phase fluid mixture, accounting for phase changes and latent and sensible heat effects. During the second part of the year, within the collaboration with the Lawrence Berkeley National Laboratory, simulations were also performed taking into account the effects of fluid circulation on stress distribution and rock deformation. This was accomplished thanks to the coupling of TOUGH2 with a commercial code for geomechanical studies, FLAC3D. The coupled TOUGH-FLAC code was developed at LBNL for the study of coupled hydrothermal-geomechanical problems. During the summer, the equation of state required to study the system at La Solfatara was implemented and the TOUGH-FLAC code was then applied to simulate the effects of short-lasting episodes of deep fluid injection into a shallow CO<sub>2</sub>-rich hydrothermal system.
- **Data acquisition**. All the simulations were performed according to a conceptual model that was developed on the basis of the available knowledge on the hydrothermal system of La Solfatara. Most of the necessary data derived from geothermal drilling and from the pre-existing geochemical model and were acquired through a bibliographic research. Important constraints for our model derived from the more recent measurement campaigns, aimed at the evaluation of diffuse degassing from La Solfatara crater. These data were used to define the order of magnitude of deep inflow and to constrain the energy budget associated with diffuse degassing.
- Data processing and interpretation After appropriate tuning of the conceptual model, performed simulations could successfully reproduce some of the main features of the hydrothermal system at La Solfatara. These include: the observed degassing rate and energy release associated with diffuse degassing, the development of a shallow single phase region,

whose existence and conditions match the predictions of the geochemical model, developed on the basis of independent data. These conditions were achieved by simulating a prolonged injection of a hot mixture of water and carbon dioxide at the base of a shallow hydrothermal system. These conditions were then applied as initial conditions to simulate chemical variations recorded during the most recent bradyseismic crises. Volcanic unrest was simulated imposing a higher fluid injection rate and a higher CO<sub>2</sub> content in the injected mixture. Appropriate choice of the periods of increased injection rate allowed us to match the observed compositional variations for the discharged fluids. A research article on these results has been recently submitted for publication. Preliminary simulations were also produced to evaluate the effects of deep fluid injection on rock deformation. Once the injection rate of hot fluids is increased, the hydrothermal system undergoes an increase of the pore pressure and temperature. This, in turn, leads to a remarkable vertical displacement at the centre of the domain. Once the fluid injection returns to the lower initial value, the deformation is relieved and a slow subsidence begins. The temporal evolution of the calculated vertical displacement well reproduces the observed ground deformation, normalized with respect to the maximum value. The coupled simulation also revealed a complex long term evolution (tens of years), associated with phase changes and phase distribution within the system, that will require a careful analysis in the future. Results from the coupled modelling will be presented in the near future at two international conferences, whose proceedings are in now preparation.

#### • RESEARCH PRODUCTS

- **3 articles published on international journals** (see below)

invited papers and talks (2):
"TOUGH2 applied to the study of hydrothermal circulation in an active volcanic system" held at the LBNL on August 2<sup>nd</sup>, 2002.
"Monitoring and modelling of diffuse degassing at La Solfatara (Italy)" held at the Earth Science Dept. University of California, Berkeley, on August 20<sup>th</sup>, 2002.

#### - presentations at international meetings (5) Todesco M., Chiodini G., Macedonio G., Modeling of diffuse gas emission in volcanic

areas. Origin Emissions and impacts of volcanic gases. London, 25-26 october 2001. Todesco M., Chiodini G., Macedonio G., Monitoring and modeling diffuse gas emission from volcanic areas. An interdisciplinary approach to assess hydrothermal system evolution. AGU Fall Meeting, 10-15 december 2001 San Francisco, CA.

- Demaria C., Todesco M., Neri A., Blasi G., Presenting numerical modelign of explosive volcanic eruption to a general public. AGU Fall Meeting, 10-15 december 2001 San Francisco, CA.
- Todesco M., Rutqvist J., Pruess K., Oldenburg C. M. Multi-phase fluid circulation and ground deformation: a new perspective on bradyseismic activity at the Phlegrean Fields (Italy). Twenty-Eighth Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, January 27-29, 2003.
- Todesco M., Rutqvist J., Chiodini G., Pruess K., Oldenburg C. M. Modeling of recent volcanic episodes at Phlegrean Fields (Italy): geochemical variations and ground deformation. TOUGH Symposium 2003, Lawrence Berkeley Nat. Lab., Berkeley, May 12-14, 2003.

PUBLICATIONS LIST (inclusive of papers in prints and accepted)

Todesco M., Neri A., Esposti Ongaro T., Papale P., Macedonio G., Santacroce R. e Longo A., (2002) Pyroclastic flow hazard at Vesuvius from numerical modelling. I. Large scale dynamics. Bull. Volcanol., 64, 155-177.

Esposti Ongaro T., Neri A., Todesco M., Macedonio G., (2002) Pyroclastic flow hazard at Vesuvius from numerical modelling. II. Analysis of local flow variables. Bull. Volcanol., 64, 178-191.
Todesco M., Chiodini G. e Macedonio G. (submitted) Monitoring and modeling hydrothermal fluid emission at La Solfatara (Phlegrean Fields, Italy). J. Volcanol. Geotherm. Res. (\*)

(\*) The paper was presented for a special issue of JVGR. It already went through the reviewing process and is accepted with minor revision, but the final decision of the editor on the entire special volume is still not official.